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Importance of Sequence of Impregnation in the Activity Development of Alkali-Promoted Mo Catalysts for Alcohol Synthesis from CO—H_2

The selective production of C_2^+ alcohols from CO and H_2 is of both commercial and academic interest in C_1 chemistry. The alcohol mixtures can be used as additives in gasoline to enhance the octane number. There are a number of reports on the catalysts for the synthesis of light alcohols (*1*, *2*). Modification of conventional methanol synthesis catalysts results in the coproduction of methanol and higher mixed alcohols (*3*). Rh is unique in its ability to catalyze the formation of C_2 oxygenates (*4*, *5*). Synthesis of alcohols on molybdenum-based catalysts, however, was not reported until our discovery that mixed alcohols were efficiently produced from CO and H_2 on alkali-promoted molybdenum catalysts (*6*). Hydrogenation of CO on Mo catalysts has long been recognized as producing mainly methane and light hydrocarbons (*7–18*). Other interesting features of Mo catalysts were that they operated well in a CO-rich gas and are resistant to sulfur poisoning. Dow Chemical recently claimed a patent (*19*, *20*) on the production of alcohols over molybdenum sulfide catalysts.

In the initial study in this laboratory (*6*), catalysts were prepared by coimpregnation of SiO_2 with KCl and Mo salts. As the Mo loading was decreased, however, we encountered a difficulty in preparing the catalyst with good reproducibility. Hence we have employed different preparations for the Mo—K/SiO_2 catalysts. In this note we report that sequence of impregnation greatly affects the activity and selectivity. A sequence in which the K is added first, followed by impregnation with $(NH_4)_6Mo_7O_{24}$, gives rise to reproducible preparation of catalysts for alcohol production.

The Mo metal loading was 5 and 10 wt% Mo. The K/Mo mole ratio was 0.4 for all the catalysts studied. Two different preparations for the Mo—KCl/SiO_2 (Fuji Davison 57, surface area = 270 m^2/g) were used. These preparations differed in the sequence in which the impregnation was carried out. Mo—KCl*/SiO_2 denotes a preparation sequence in which the KCl was added first, followed by air calcination at 673 K for 1 h and impregnation with $(NH_4)_6Mo_7O_{24}$ solution. Mo*—KCl/SiO_2 denotes the reverse sequence; Mo was added first, followed by drying at 393 K and impregnation with KCl solution. Catalysts were treated in flowing He at 673 K for 1 h and then reduced in flowing H_2 at 773 K for 12 h. The synthesis reaction was carried out in a stainless steel tubular reactor containing 1.0 g catalyst in a flow system. Activity/selectivity data were obtained over a period of 50–130 h until steady-state levels were attained. Analyses of the products were based on gas chromatographs using four columns. The XPS spectra of supported catalysts were recorded on a Shimadzu electron spectrometer ESCA 750 with Mg$K\alpha$ excitation radiation. Sample preparation for XPS measurements was performed in a globebox filled with nitrogen. The catalytic surface areas of reduced, supported Mo catalysts were measured by O_2 adsorption at 195 K (*21*, *22*). Details have been described in Ref. (*23*). After measuring the O_2 adsorption, each sample was subjected to oxygen titration; oxygen was admitted to the chemisorption cell at about 300 Torr and sam-

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TABLE 1

Initial and Steady-State Activities over Mo/SiO_2 Catalysts[a]

Catalyst	Initial				Steady state				
	CO conv. (%)	CO_2 yield (%)	Selectivity for alcohols[b] (C-atom%)	C_2^+ alcohols in alcohols (C-atom%)	Time on stream (h)	CO conv. (%)	CO_2 yield (%)	Selectivity for alcohols[b] (C-atom%)	C_2^+ alcohols in alcohols (C-atom%)
5 wt% Mo—KCl*/SiO_2[c]	1.7	0.9	24	56	130	3.3	1.4	39	55
5 wt% Mo*—KCl/SiO_2[d]	3.8	2.0	15	55	50	10.9	5.1	9	73
10 wt% Mo—KCl*/SiO_2[c]	2.6	1.2	42	61	100	5.6	2.3	49	63
10 wt% Mo*—KCl/SiO_2[d]	3.5	1.8	33	68	50	4.5	2.1	39	61
10 wt% Mo/SiO_2	9.7	4.8	0.5	25					

[a] Reaction conditions; 573 K, 1.6 MPa, $H_2/CO = 1$, W/F = 10 g-cat h/mol.
[b] CO_2-free basis.
[c] Denotes impregnation with KCl first.
[d] Denotes impregnation with $(NH_4)_6Mo_7O_{24}$ first.

ple was heated stepwise up to 773 K. The final equilibrated O_2 pressure was >50 Torr. The original oxidation number of the Mo could then be calculated from the total amount of O_2 consumed, assuming that Mo(VI) was the final product (*24*). X-Ray powder diffraction measurements were performed using a Rigaku Denki diffractometer RU-200A with Cu*Kα* radiation.

Initial and steady-state CO conversions and alcohol selectivities are listed in Table 1 for the series of 5 and 10 wt% Mo—KCl/SiO_2 catalysts. As is expected from the CO shift activity of the Mo catalysts (*8–16, 18*), almost all of the oxygen leaves the reactor as CO_2 rather than H_2O. The alcohol selectivity (C-atom %) in Table 1 is given on a CO_2 free basis. Initial alcohol selectivity of 5 wt% Mo—KCl*/SiO_2 was significantly higher than that of 5 wt% Mo*—KCl/SiO_2. For 5 wt% Mo—KCl*/SiO_2, both alcohol selectivity and CO conversion were gradually increased with time on stream. This is contrasted with the behavior of Mo*—KCl/SiO_2, over which the alcohol selectivity was decreased since hydrocarbon production was overwhelmingly increased. At the steady state the alcohol selectivity of Mo—KCl*/SiO_2 was more than four times higher than that of Mo*—KCl/SiO_2. Similar effect was also observed for 10 wt% Mo—KCl/SiO_2 catalysts, although the difference in selectivity for alcohol was somewhat lessened, compared to 5 wt% Mo—KCl/SiO_2. It should be noted that, with increasing reaction pressure to 5.0 MPa, the alcohol selectivity over 10 wt% Mo—KCl*/SiO_2 was improved to 63%, at 10% of CO conversion.

Amount of O_2 adsorption uptake and apparent oxidation number of the Mo after reduction are shown in Table 2 for the 10 wt% Mo catalysts. O_2 uptake for the reduced molybdenum oxides decreased in the following order: $Mo/SiO_2 \gg$ Mo*—KCl/SiO_2 > Mo—KCl*/SiO_2. Apparent oxidation number decreased in the order Mo—KCl*/SiO_2 > Mo*—KCl/SiO_2 > Mo/SiO_2. Thomas *et al.* reported that the major part of the Mo species supported on SiO_2 was reduced at a lower temperature than

TABLE 2

O_2 Uptakes and Apparent Oxidation Number of 10 wt% Mo/SiO_2 Catalysts

Catalyst	Net O_2 uptake following reduction[a] (μmol/g-cat)	Apparent oxidation number following reduction[b]	Net O_2 uptake following reaction[a] (μmol/g-cat)
Mo—KCl*/SiO_2[c]	122	2.09	23
Mo*—KCl/SiO_2[d]	145	1.95	35
Mo/SiO_2	500	1.26	199

[a] Measured at 195 K, according to Refs. (*19, 20*).
[b] Estimated from O_2 consumption from 195 to 773 K.
[c] Denotes impregnation with KCl first.
[d] Denotes impregnation with $(NH_4)_6Mo_7O_{24}$ first.

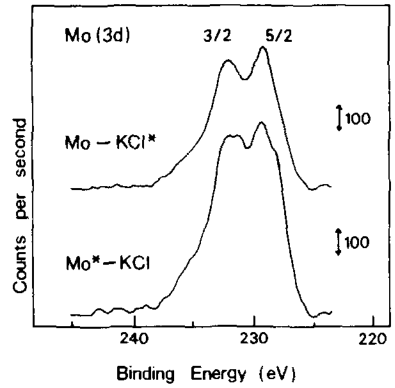

FIG. 1. Molybdenum (3*d*) ESCA region of Mo—KCl*/SiO_2 and Mo*—KCl/SiO_2 catalysts after reduction.

unsupported MoO_3 (*25*). It is speculated that the interaction of Mo oxides with SiO_2 promotes their reduction. The presence of KCl seems to retard the reduction, especially when KCl is added to SiO_2 prior to $(NH_4)_6Mo_7O_{24}$. First addition of KCl may lead to the decrease in the number and change in the property of SiO_2 sites capable of interacting with Mo species. The presumed decrease in the interaction is reflected in the decrease in O_2 uptake from which the degree of Mo dispersion could be estimated. Increase in Mo loading with K/Mo kept constant should result in the increase in the amount of Mo species which is not directly interacted with the support. As would be expected, with increasing Mo loading, alcohol selectivity was increased irrespective of the sequence of impregnation, and became less sensitive to the different ways of catalyst preparation. O_2 uptake measurements indicated lower dispersion at higher Mo loading; the dispersion of 10 and 20 wt% Mo—KCl*/SiO_2 assuming O/Mo = 1 was estimated to be 23 and 12%, respectively. It should be also recognized that there is a possibility that K inherently influences the reduction behavior of Mo; Kantschewa *et al.* have found that the presence of K decreases the reducibility of the Mo supported on Al_2O_3 (*26*).

The higher initial selectivity for alcohols seems to be correlated with the higher apparent oxidation number of the Mo following reduction. This is in agreement with the effect of increasing the reduction temperature to 873 K, which resulted in the drastic decrease in alcohol production and increase in hydrocarbon formation. Extensive reduction of Mo occurred when $MoO_2(acac)_2$(acacH = acetylacetone) was used as the Mo precursor, giving a highly active hydrocarbon-forming catalyst (*23*). These results are consistent with the observation by Saito and Anderson, who showed that activity of Mo for CO hydrogenation producing hydrocarbons increased with decreasing oxidation state (*8*). Figure 1 shows the XPS spectra of 10 wt% Mo—KCl/SiO_2 catalysts after reduction. The Mo*—KCl/SiO_2 gave the $Mo3d_{5/2}$ shoulder peak at low binding energies (228.1 eV), which was absent in the Mo—KCl*/SiO_2. This fact suggests that the Mo*—KCl/SiO_2 contains more extensively reduced Mo species.

The drastic decrease in O_2 uptake of the used catalysts indicates that degree of dispersion of Mo reduced during the CO—H_2 reaction. The XRD observation of the used 10 wt% Mo—KCl*/SiO_2 catalyst identified MoO_2 as the major phase; lines corresponding to metallic Mo were very weak. On the contrary, the used Mo*—KCl/SiO_2 showed relatively strong bands characteristic of metallic Mo. This again indicates the close relationship between the hydrocarbon formation and low valent Mo such as metallic Mo.

As we reported previously (*6*), Mo—K_2CO_3/SiO_2 prepared by coimpregnation favored hydrocarbon production. However, we have found that the alcohol selectivity can be similarly improved by impregnating SiO_2 with K_2CO_3 first. Steady-state selectivity for alcohol over 10 wt% Mo—$K_2CO_3^*/SiO_2$ proved 34% at 6.8% of CO conversion. Thus the remarkable effect of KCl on increasing alcohol production, compared to K_2CO_3, may be partly due to its greater ability to prevent Mo species from interacting with SiO_2.

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